PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B41M 7/00, 5/00

A1

(11) International Publication Number: WO 95/30547

(43) International Publication Date: 16 November 1995 (16.11.95)

(21) International Application Number: PCT/US95/05369

(22) International Filing Date: 1 May 1995 (01.05.95)

(30) Priority Data:
08/239,815 9 May 1994 (09.05.94) US

(71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US).

(72) Inventors: BUGNER, Douglas, Eugene; 148 Augustine Street, Rochester, NY 14613 (US). GARMAN, Douglas, Edward; 1245 Stafford Crescent, Webster, NY 14580 (US).

(74) Agents: MONTGOMERY, Willard, G. et al.; 343 State Street, Rochester, NY 14650-2201 (US).

(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: RECORDING PROCESS

(57) Abstract

A recording process is provided for producing recorded images having enhanced durability. The process includes a lamination step in which a transparent protective resin film is bonded or adhered to the surface of an ink-receiving layer of an ink-recording medium containing a recorded image in which the ink-receiving layer comprises a hydrophilic or hydrophobic resin which is capable of bonding or adhering the transparent protective resin film to the recorded image surface of the ink-receiving layer upon the application of heat and pressure to the transparent protective resin film and the ink-recording medium.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

RECORDING PROCESS

The present invention relates to a method of protecting a print formed by recording an image on a recording medium by a recording process which employs as a recording liquid, an ink, especially an ink-jet recording process.

The ink-jet recording process is a process for performing recording on a recording medium in which droplets of a recording liquid, that is, an ink, are ejected or propelled from a print head having one or more orifices onto the recording medium.

The recording liquid, or ink, generally comprises a recording agent such as a dye or a pigment and a solvent. The solvent typically is either water or a mixed solvent of water and other water miscible solvents such as polyhydric alcohols.

In ink-jet recording, numerous schemes are utilized to control the deposition of the ink droplets onto the image-recording medium to yield the desired image. In one process, known as continuous ink-jet recording, a continuous stream of droplets is charged and deflected in an image-wise manner onto the surface of the image-recording medium, while unimaged droplets are caught and returned to an ink sump. In another process, known as drop-on-demand ink-jet recording, individual ink droplets are projected as needed onto the image-recording medium to form the desired image. Common methods of controlling the projection of ink droplets in drop-on-demand printing include piezoelectric transducers and thermal bubble formation. Ink-jet recording is rapidly gaining acceptance by the public as a recording process because it generates little noise and permits economical and multi-color printing.

The recording media used in ink-jet recording processes typically comprise an ink-receiving layer provided on a support. The recording media include those intended for reflection viewing, which usually have an opaque support, and those intended for viewing by transmitted light, which usually have a transparent or translucent support.

A wide variety of different types of ink-receiving layers have been proposed heretofore. For example, U.S.-A- 4,868,581 and U.S.-A- 4,956,223 describe ink-receiving layers consisting of albumin, gelatin, caesin, starch, cationic starch, gum arabic, sodium alginate, poly(vinyl alcohol), poly(amide), poly(acrylamide), poly(vinylpyrrolidone), a quaternized poly(vinylpyrrolidone), poly(ethyleneimine), poly(vinylpyridinium halide), melamine resins, poly(urethanes), polyesters, carboxymethyl cellulose, a SBR latex, an NBR latex, poly(vinyl formal), poly(vinyl methacrylate), poly(vinyl butyral), poly(acrylonitrile), poly(vinyl chloride), poly(vinyl acetate), a phenolic resin, an alkyd resin, poly (methyl methacrylate) and the like.

In general, when such media are imaged with inks, good quality text and graphic images can be generated. However, the recorded images are not always satisfactory in terms of durability. That is, it is also desirable that the recorded images be abrasion-resistant so that they are not easily rubbed off, smear resistant, so that they can be subjected to normal handling without risk of smearing, lightfast so that they can be displayed for long periods of time without noticeable fading or shifting of colors, and waterfast, so that they are not harmed by contact with water or other aqueous liquids which might come into contact with the recording media as a result of spills or other

accidental exposure to liquids. The recorded image and the ink-receiving layer in general also should be non-blocking to facilitate packaging and handling.

A means for achieving these objectives has been proposed in U.S.-A- 4,809,451 where a print holder is provided for preserving a print in which the print is sandwiched between upper and lower adhesive-bearing plates. The upper plate has an opening through which the print can be observed and in which a transparent film can be laid over the print either below or above the upper plate. This method of protecting the print, however, is unduly cumbersome and expensive.

Thus, it can be seen that a need still exists in the art for providing a simple, inexpensive and readily implementable means for providing a recorded image having enhanced abrasion resistance, enhanced smear resistance, enhanced light-fastness, enhanced waterfastness and enhanced anti-blocking characteristics. The present invention provides such a process.

In accordance with the present invention, it has now been found that certain of the resins which previously were used to form the ink-receiving layers of ink-recording media used in ink-jet recording processes for absorbing and fixing the recording liquids, that is, the inks deposited thereon, also are capable of bonding or adhering such ink-receiving layers to a transparent protective resin film uniformly applied over and on the surface of such ink-receiving layers simply by applying heat and pressure to the composite formed by the transparent protective resin film and the ink-recording medium. It has specifically been found that certain of the previously used naturally occurring water-soluble hydrophilic resins and certain of the previously used synthetic

hydrophilic and hydrophobic resins are capable of bonding an ink-receiving layer comprising or containing such a resin to a transparent protective resin film where the ink-receiving layer is contacted therewith and heat and pressure are subsequently applied to the composite formed by the transparent protective resin film and the ink-receiving layer. As a result, the print is easily and inexpensively preserved with good durability without resorting to mounting the print in a complicated print holder such as the one disclosed in the aforementioned patent, U.S.-A- 4,809,451.

Thus, there is now provided an ink-jet recording process which comprises the steps of:

(1) applying droplets of ink in an image-wise fashion onto the surface of an ink-receiving layer of an ink-recording medium to record an image thereon wherein the ink-recording medium comprises an ink-receiving layer provided on a transparent or opaque support;

(2) contacting the surface of the ink-receiving layer containing the recorded image with a transparent protective resin film to form a composite of the ink-recording medium and the transparent protective resin film, and

(3) applying temperature and pressure to the composite thus formed sufficient to adhere or bond the ink-receiving layer of the ink-recording medium to the transparent protective resin film wherein the ink-receiving layer comprises at least one hydrophilic or hydrophobic resin capable of adhering or bonding the ink-receiving layer to the transparent protective resin film upon the application of heat and pressure to the composite.

The ink-jet recording medium used in the ink-jet recording process of the present invention is

characterized primarily by its ink-receiving layer which comprises any suitable hydrophilic or hydrophobic ink-receptive resin or polymer or a blend of such resins or polymers, which can be coated onto a support material to yield an absorbent layer capable of being imaged by an ink-jet printing device and which is capable of adhering or bonding the ink-receiving layer to a transparent protective resin film applied over the surface of the ink-receiving layer after an image has been recorded on the surface of the ink-receiving layer upon the application of heat and pressure to the composite formed by the ink-jet recording medium overlaid with the transparent protective resin film.

The term "hydrophilic", as used herein, is used to describe a material that is generally receptive to water, either in the sense that its surface is wettable by water or an aqueous fluid, that is, a fluid which contains substantial amounts of water, or in the sense that the bulk of the material is able to absorb significant quantities of water or an aqueous fluid.

The term "hydrophobic," as used herein, is used to describe a material that is substantially insoluble and non-swellable in water or an aqueous fluid. More specifically, materials that exhibit surface wettability by water or an aqueous fluid are said to have hydrophilic surfaces, while materials that have surfaces that are not wettable by water or an aqueous fluid are said to have hydrophobic surfaces.

The recording medium generally comprises a substrate or a support as a supporting member and a recording face provided on a surface of the substrate or support, namely the ink-receiving layer. When the image generated by the ink-jet recording process is desired to be in the form of a reflection print for surface image observation, the support is opaque. When

the image generated by the ink-jet recording process is desired to be viewed with transmitted light, the support is transparent. A transparent support is particularly advantageous for use in viewing by projection as in the case of overhead projection. In this application, the ink-receiving layer must also be substantially transparent.

In either case, the ink-receiving layer comprises or contains at least one hydrophilic or hydrophobic ink-receptive resin or polymer which can be coated onto a support material to yield an absorbent layer capable of being imaged by an ink-jet printing device and which is capable of bonding or laminating the ink-receiving layer to a transparent protective resin film placed on the ink-receiving layer after an image has been recorded on the surface of the ink-receiving layer upon the application of heat and pressure to the composite formed by the ink-recording medium and the transparent protective resin film.

The hydrophilic or hydrophobic polymer or resin comprises the major component of the ink-receiving layer. Typically, the resin or polymer comprises at least 40 percent by weight of the ink-receiving layer to insure that an adequate amount of the resin is present in the ink-receiving layer to bond the ink-receiving layer to the transparent protective resin film applied over it. Such polymers or resins are generally non-tacky and non-adhesive under ambient conditions, but when subjected to heat they become quite tacky and adhesive. That is to say these resins or polymers are advantageously heat activatable and become self-adhesive or self-adherent at elevated temperatures. In essence, these materials function as hot melt adhesives when subjected to sufficient heat.

If desired, the entire ink-receiving layer may be comprised of such a resin or polymer.

Examples of suitable naturally occurring water-soluble hydrophilic resins or polymers which can be used to form the ink-receiving layers of the ink-recording media used in the present invention which have a high degree of ink absorbency include naturally occurring water-soluble hydrophilic resins such as albumin, gelatin, casein, starch, cationic starch, gum arabic, sodium alignate. Examples of synthetic water-soluble hydrophilic resins or polymers which can be used to form the ink-receiving layers of the ink-recording media used in the present invention include poly(vinyl alcohol), poly(amide), poly(acrylamide), poly(vinylpyrrolidone), poly(ethyleneimine), poly(vinylpyridinium halide), melamine resins, poly(urethanes) and polyesters. In addition to the above-described thermoplastic resins, it is possible to include hydrophobic resins such as styrene-butadiene rubbers, acrylonitrile-butadiene rubbers, poly(vinyl formal), poly(methyl methacrylate), poly(vinyl butyral), poly(acrylonitrile), poly(vinyl chloride), poly(vinyl acetate) and the like. Other hydrophilic and hydrophobic resins or polymers additional to those described above which can be used in the practice of the present invention can easily and readily be determined by those skilled in the art.

In a particularly preferred embodiment, a polymer or resin having a high degree of ink-absorbency is used for forming the ink-receiving layer and since an ink-jet recording method generally employs an aqueous ink, as the polymer or resin used for forming the ink-receiving layer, it is preferable to use a polymer having good ink absorbency with respect to an

aqueous ink, for example, one of the water-soluble or hydrophilic polymers in the above-described polymers.

A particularly suitable ink-receiving layer for use in the recording media used in the present invention is a layer which is coated onto a support as an aqueous dispersion of particles of a polyester ionomer, namely, a poly(cyclohexylenedimethylene isopthalate-co-sodiosulfobenzenedicarboxylate) dispersed in a vinyl pyrrolidone polymer as disclosed in U.S.-A- 4,903,040.

Another particularly suitable ink-receiving layer for use in the recording media used in the present invention is a layer which is coated onto a support as an aqueous dispersion of particles of a polyester ionomer, namely a poly(cyclohexylenedimethylene-co-oxydiethylene isopthalate-co-sodiosulfobenzenedicarboxylate), dispersed in a vinyl pyrrolidone polymer as disclosed in U.S.-A- 4,903,039.

Still another particularly suitable ink-receiving layer for use in the recording media used in the present invention is a layer which is coated onto a support as an aqueous dispersion of particles of a polyester ionomer, namely a poly[cyclohexylenedimethylene-co-xylylene terephthalate-co-malonate-co-sodioiminobis(sulfonylbenzoate)] dispersed in a vinyl pyrrolidone polymer as disclosed in U.S.-A- 4,903,041.

The particles of polyester generally have a diameter of up to 1 micrometer, often 0.001 to 0.1 and typically 0.01 to 0.08 micrometer. The size of the polyester particles in the ink-receiving layer is compatible with the transparency requirements of the ink-receiving layer. The ratio, by weight of polyester to vinyl pyrrolidone polymer in the ink-receiving layer

typically is at least 1:1 and generally is in the range of 1:1 to 6:1.

The ink-receiving layers used in the recording media used in the present invention also can incorporate various known additives, including matting agents such as titanium dioxide, zinc oxide, silica and polymeric beads such as crosslinked poly(methyl methacrylate) or polystyrene beads for the purposes of contributing to the non-blocking characteristics of the recording media used in the present invention and to control the smudge resistance thereof; surfactants such as non-ionic, hydrocarbon or fluorocarbon surfactants or cationic surfactants, such as quaternary ammonium salts for the purpose of improving the aging behavior of the ink-absorbent resin or layer, promoting the absorption and drying of a subsequently applied ink thereto, enhancing the surface uniformity of the ink-receiving layer and adjusting the surface tension of the dried coating; fluorescent dyes; pH controllers; anti-foaming agents; lubricants; preservatives; viscosity modifiers; dye-fixing agents; waterproofing agents; dispersing agents; UV absorbing agents; mildew-proofing agents; antistatic agents, and the like. Such additives can be selected from known compounds or materials in accordance with the objects to be achieved. It should be noted however that when the image generated by the ink-jet recording process is desired to be viewed with transmitted light where the support is transparent, the type and amount of additives chosen must be such that the ink-receiving layer itself remains light transmissive or transparent, that is, substantially non-light-scattering. In this case, therefore, care must be exercised in the selection and amounts of additives which are included in the ink-receiving layers so that the ink-receiving

layers remain clear and transparent and are not rendered cloudy or hazy.

Particularly preferred ink-receiving layers for use in the recording media used in the present invention are layers which are coated onto a support as an aqueous dispersion of 50 to 70 weight percent of a water-dispersible polyester ionomer of the type disclosed and described in the above mentioned U.S.-A-4,903,039, U.S.-A- 4,903,040 and U.S.-A- 4,903,041, 25 to 50 weight percent of poly(vinyl pyrrolidone), 0 to 5 weight percent of a homopolymer or a copolymer of an alkylene oxide containing from 2 to 6 carbon atoms, as a surface active agent, 0 to 5 weight percent of poly(vinyl alcohol), .01 to 3.0 weight percent poly(methyl methacrylate-co-divinylbenzene) particles having an average particle size of 3 to 30 micrometers to enhance the smoothness of the ink-receiving layer, 0.1 to 1.0 weight percent of propylene glycol butyl ether as a surfactant to provide an ink-receiving layer having a uniform thickness and 90 weight percent water. The polymerized alkylene oxide components constitute nonionic surface active polymers including homopolymers and copolymers of an alkylene oxide in which alkylene refers to carbon linkages such as ethylene, propylene, butylene and the like and are characterized by molecular weights of from 100,000 to 5,000,000 weight average molecular weight. Poly(ethylene oxide) is a particularly preferred poly(alkylene oxide).

The ink-receiving layer is conveniently applied to the support material by deposition from a solution or dispersion of the hydrophilic resin or polymer and other additives as mentioned above, if desired, in a volatile medium, such as an aqueous or organic solvent medium in accordance with known coating procedures such as immersion or dip coating, roll

coating, reverse roll coating, air knife coating, doctor blade coating, bead coating and curtain coating, followed by drying as rapidly as possible with a dryer such as a hot-air dryer or a hot-air oven, a hot drum or the like.

The ink-receiving layer may have a dry thickness sufficient for absorbing and capturing the recording liquid or ink, which may range, though variable depending on the amount of recording liquid, from 1 to 30 micrometers, preferably from 5 to 20 micrometers.

The support materials utilized in the recording media used in the present invention may be transparent or opaque materials, as desired. Examples of useful support materials include paper, cloth, wood, metallic sheet materials, plastic film and glass. Most typically, paper is used where an opaque support is desired, and plastic film is used where a transparent support is desired. For the preparation of transparent recording media, the support can be composed of cellulose esters, such as cellulose triacetate, cellulose acetate propionate or cellulose acetate butyrate, polyesters such as poly(ethylene terephthalate), polyamides, polyimides, polycarbonates, polyolefins, poly(vinyl acetals), polyethers, poly(vinyl chloride) resins, polysulfonamides, glass and the like. Polyester supports, and especially poly(ethylene terephthalate), are preferred because of their excellent dimensional stability characteristics. The support must be transparent if used for overhead image projection and, if transparent, may contain known additives including UV light absorbers to filter out ultraviolet light so as to enhance the lightfastness of the recorded image. The UV absorber should be capable of absorbing light mainly in the 250 to 400 nanometer

region from the light penetrating the transparent support. The light in this wavelength range is mainly responsible for the decomposition and deterioration of the dyes used as recording agents in recording liquids, thereby discoloring, fading or bleaching the image. The following compounds can be cited as suitable ultraviolet absorbers: 2,2'-dihydroxy-4-dimethoxybenzophenone (Cyasorb UV-24 available from ACC); benzophenone compounds such as 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Uvinul D-49 available from BASF); 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, (Tinuvin P available from Ciba Geigy); 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole (Tinuvin PS available from Ciba Geigy); 2-(2'-hydroxy-3', 5'-di-tert-butylphenyl)benzotriazole (Tinuvin 320 available from Ciba Geigy); 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole (Tinuvin 326 available from Ciba Geigy); phenyl salicylate (Seesorb 201 available from Nisseki Calcium); p-tert-butylphenyl salicylate (Sumisorb 90 available from Sumitomo Chemical) and salicylic acid compounds such as p-octylphenyl salicylate (OPS available from Eastman Chemical).

In addition, the support must be self-supporting. By "self-supporting" is meant a support material such as a sheet or film that is capable of an independent existence in the absence of a supporting substrate. The support is suitably of a thickness of from 10 micrometers to 250 micrometers, preferably from 25 micrometers to 125 micrometers, when it is transparent and from 75 micrometers to 250 micrometers when it is opaque. If desired, in order to promote adhesion of the ink-receiving layer to the polymeric support, the surface of the support may first be treated with a chemical priming medium as is generally

known in the art. Examples of such conventional priming or adhesion promoting agents for forming a priming layer on the surface of the support include halogenated phenols or partially hydrolyzed vinyl chloride-vinyl acetate copolymers. Such a copolymer conveniently contains from 60 to 98 percent of vinyl chloride and from 0.5 to 3 percent of hydroxyl units, by weight, of the copolymer. The molecular weight (number average molecular weight) of the copolymer is in a range of from 10,000 to 30,000 and preferably from 16,500 to 25,000.

The priming agent suitably is applied at a concentration level which will yield a priming layer having a relatively thin dry coat thickness, for example, generally less than 2, and preferably less than 1, micrometer. Alternatively, the support surface may be corona-discharged-treated prior to applying the ink-receiving layer to the support surface in order to promote adhesion of the ink-receiving layer to the support.

The transparent protective resin film which is bonded to the ink-receiving layer according to the ink-jet recording process of the present invention provides excellent abrasion resistance, smear resistance, waterfastness, lightfastness and anti-blocking properties to the image or print recorded on the ink-receiving layer of the recording media used in the practice of the recording process of the present invention. The transparent protective film is placed directly over the printed or image-containing surface of the ink-receiving layer of the ink-recording medium so that it is in contact with and entirely covers the printed surface. The transparent protective film or sheet conforms in size and shape to the recorded image surface so that it is in good agreement with and

entirely covers the image-containing surface of the ink-receiving layer and forms a composite with the ink-recording medium. The transparent protective film is then bonded or laminated to the image-containing ink-receiving layer by applying heat and pressure to the composite film and ink-recording medium using an ordinary laminating device such as a flat bed press or a roller press as described in detail below. In this manner, the recorded image or print is positioned beneath the transparent protective film and thereby protected against abrasion, smearing, fading and damage by water. Also, the transparent protective film imparts good anti-blocking properties to the recorded image and the ink-recording medium in general.

The transparent protective resin film is constituted wholly or mainly of a thermoplastic resin such as ethyl cellulose vinyl acetate resin and their derivatives, polystyrene, polyethylene, ethelene-vinyl acetate copolymers, polyisobutylene, hydrocarbon resins, polypropylene, polyamide resins and polyester resins. If desired, the transparent protective resin film or layer may contain additives, examples of which may include plasticizers, tackifiers, antioxidants, ultraviolet light absorbers to prevent or retard the recorded image from fading, discoloring or bleaching, antistatic agents and the like.

Adhesion of the transparent protective film to the ink-receiving layer is achieved through a lamination step or process in which sufficient heat and pressure are applied to the composite formed by the transparent protective film and the image-recording medium to bond or adhere the transparent protective film to the ink-receiving layer. Conditions such as time, temperature and pressure will vary depending upon the particular materials which are selected for use as

the thermoplastic protective transparent resin and the ink-receiving layer. Such conditions can easily and readily be determined by one skilled in the art without undue experimentation. Typically, if a roller press is utilized the composite can be passed through a pair of nip rollers under a pressure of from 2.0 to 20 psi preferably 5.0 to 15 psi, at a speed of 24 inches (60.96 cm) per minute when the roller adjacent the support is heated to a temperature of 100°C and the roller adjacent the transparent protective film is heated to 90°C. Any suitable commercially available laminating device may be used. Such laminating devices may be in the form of a flat-bed press, for example, or a roller press as mentioned previously. In a flat-bed press, the composite is heated all at once under pressure for a time sufficient to achieve adequate adhesion. In a roller press, the composite is fed between a pair of heated rollers under pressure. The movement and friction of the rollers causes the composite to incrementally pass through the nip formed by the two rollers. The speed of the rollers is adjusted to provide a sufficient time in the nip to achieve adequate adhesion. The thermoplastic resin layer should be prepared so that its shrinkage ratio due to its change in temperature after the lamination step will be about the same as the shrinkage ratio of the print and will not cause the laminated print to curl.

The dry thickness of the transparent protective resin film or layer should be in a range of from 0.01 to 200 micrometers, preferably from 5 to 100 micrometers.

The inks used to image the recording media used in the present invention are well-known inks. The ink compositions used in ink-jet printing typically are

liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, preservatives, and the like. The solvent or carrier liquid can be comprised solely of water or can be predominantly water mixed with other water miscible solvents such as polyhydric alcohols, although inks in which organic materials such as polyhydric alcohols are the predominant carrier or solvent liquid also may be used. Particularly useful are mixed solvents of water and polyhydric alcohols. The dyes used in such compositions are typically water-soluble direct or acid type dyes. Such liquid ink compositions have been described extensively in the prior art including for example, U.S.-A- 4,381,946; U.S.-A- 4,239,543 and U.S.-A- 4,781,758.

The invention is further illustrated by reference to the following examples.

Example 1

An ink-receiving layer comprising 6.59 weight percent poly[1,4-cyclohexylenedimethylene-co-p-xylylene (40/60) terephthalate-co-malonate-co-3,3'-sodio-iminobis(sulfonylbenzoate)] (obtained from Eastman Chemical Company as AQ38S), 2.83 weight percent poly(vinyl pyrrolidone (supplied by BASF Corporation under the tradename Kollidon 90), 0.2 weight percent poly(ethylene oxide obtained from Aldrich Chemical Company), 0.2 weight percent poly(vinyl alcohol) (sold by Air Products and Chemicals under the tradename AIRVOL 165), 0.07 weight percent poly(methyl methacrylate-co-divinylbenzene) particles having an average particle size of 5 micrometers, 0.11 weight percent propylene glycol butyl ether (obtained from Union Carbide Corporation under the tradename Propasol-

B), and 90.0 weight percent distilled water was applied to an opaque support comprising a 6.6 mil thick photographic paper support overcoated with a 1.28 mil layer of poly(ethylene terephthalate) at a dry laydown coverage of 1.5 g/ft^2. The support was corona-discharge-treated just prior to the application of the coating solution. The ink-receiving layer was imaged with a Hewlett Packard Desk Writer 550C 4-color ink-jet printer. A clear, transparent protective layer comprising a sheet of Kodak Diconix Ink-Jet Transparency Material, Catalog No. 140,4540 obtained from Eastman Kodak Company, Rochester, New York, conforming in size and shape to the recorded image-bearing surface of the ink-receiving layer was superposed over the recorded image surface to form a composite of the transparent protective resin film and the supported ink-receiving layer. The composite thus formed was passed through a pair of heated rollers at a rate of 24 inches (60.96 cm) per minute. The top roller which was 3 inches (7.62 cm) in diameter and was adjacent to the support was heated to 100°C and the bottom roller which was 3 inches (7.62 cm) in diameter and which was adjacent to the transparent protective film was heated to 90°C. The laminated composite exhibited excellent adhesion. Attempts to manually separate the transparent protective resinous film from the ink-receiving layer were unsuccessful.

The same transparent protective layer was shown to be non-adhesive when attempts were made to laminate it directly to a sample of the same photographic paper support as described above which had not been overcoated with a layer of a resin as described and disclosed herein under the same laminating conditions as described above.

Although the present invention is directed primarily towards a process for producing recorded images having enhanced durability in which the recorded images are produced by means of an ink-jet printer in which droplets of ink typically are ejected through one or more orifices of a print head onto an ink-recording media of the type described herein, images which have been recorded on the surface of an ink-receiving layer of an ink-recording media of the type described herein by means of a pen plotter which operates by writing directly on the surface of the ink-receiving layer using a pen typically consisting of a bundle of capillary tubes in contact with an ink resevior having enhanced durability also can be produced in the same manner as those images produced by an ink-jet printer. That is, after an image has been created or recorded on the ink-receiving layer of an ink-recording medium of the type described herein by means of a pen plotter, a transparent protective resin film can then be superposed over the recorded image and the composite thus formed consisting of the protective film and recording medium can be subjected to heat and pressure sufficient to laminate the protective film to the ink-receiving layer of the recording medium.

CLAIMS:

1. A recording process which comprises the steps of:

(1) applying droplets of ink in an image-wise fashion onto the surface of an ink-receiving layer of an ink-recording medium to record an image thereon, said ink-recording medium comprising said ink-receiving layer provided on a transparent or opaque support;

(2) contacting the surface of said ink-receiving layer containing said recorded image with a transparent protective resin film to form a composite of said ink-recording medium and said transparent protective resin film, and

(3) applying temperature and pressure to the composite thus formed sufficient to adhere or bond said ink-receiving layer of said ink-recording medium to said transparent protective resin film, said ink-receiving layer comprising at least one hydrophilic or hydrophobic resin capable of adhering or bonding said ink-receiving layer to said transparent protective resin film upon the application of heat and pressure to said composite.

2. A recording process as claimed in Claim 1, wherein said resin is a water-soluble, hydrophilic resin.

3. A recording process as claimed in Claim 2, wherein said water-soluble, hydrophilic resin is poly(vinyl alcohol).

4. A recording process as claimed in Claim 2, wherein said water-soluble, hydrophilic resin is poly(vinylpyrrolidone).

5. A recording process as claimed in Claim 2, wherein said water-soluble, hydrophilic resin comprises a polyester.

6. A recording process as claimed in Claim 5, wherein said polyester is a poly(cyclohexylenedimethyelene isopthalate-co-sodiosulfobenzenedicarboxylate).

7. A recording process as claimed in Claim 5, wherein said polyester is a poly(cyclohexylenedimethyelene-co-oxydiethylene isopthalate-co-sodiosulfobenzene-dicarboxylate).

8. A recording process as claimed in Claim 5, wherein said polyester is a poly[cyclohexylenedimethylene-co-xylylene terephthalate-co-malonate-co-sodio-iminobis(sulfonylbenzoate)].

9. A recording process as claimed in Claim 5, wherein the polyester is poly[cyclohexylenedimethylene-co-p-xylylene terephthalate-co-malonate-co-3,3'-sodioiminobis(sulfonylbenzoate).]

10. A recording process as claimed in Claim 6, wherein the polyester comprises particles of a poly(cyclohexylenedimethyelene isopthalate-co-sodiosulfobenzenedicarboxylate) dispersed in a vinylpyrrolidone polymer.

11. A recording process as claimed in Claim 7, wherein the polyester comprises particles of a poly(cyclohexylenedimethyelene-co-oxydiethylene isopthalate-co-sodiosulfobenzenedicarboxylate) dispersed in a vinylpyrrolidone polymer.

12. A recording process as claimed in Claim 8, wherein the polyester comprises particles of a poly[cyclohexylenedimethylene-co-xylylene terephthalate-co-malonate-co-sodioiminobis(sulfonylbenzoate)].

13. A recording process as claimed in Claim 9, wherein the polyester comprises particles of a poly[1,4-cyclohexylenedimethylene-co-p-xylylene (40/60) terephthalate-co-malonate-co-3,3'-sodioiminobis-(sulfonylbenzoate)] dispersed in a vinylpyrrolidone polymer.

14. A recording process as claimed in Claim 1, wherein the ink-receiving layer is coated onto the support as an aqueous dispersion of 50 to 70 weight percent of poly[1,4-cyclohexylenedimethylene-co-p-xylylene (40/60) terephthalate-co-malonate-co-3,3'-sodioiminobis-(sulfonylbenzoate)], 25 to 50 weight percent of poly(vinylpyrrolidone), 0 to 5 weight percent of a homopolymer or a copolymer of an alkylene oxide containing from 2 to 6 carbon atoms, 0-5 weight percent of poly(vinyl alcohol), 0.1 to 3.0 weight percent poly((methyl methacrylate-co-divinylbenzene), 0.1 to 1.0 weight percent propylene glycol butyl ether and 90.0 weight percent distilled water.

15. A recording process as claimed in Claim 1, wherein the support is paper.

16. A recording process as claimed in Claim 1, wherein the support is a polyester film.

17. A recording process as claimed in Claim 16, wherein the polyester is poly(ethylene terephthalate).

18. A recording process as claimed in Claim 1, wherein the dried thickness of the ink-receiving layer is from 1 to 30 micrometers.

19. A recording process as claimed in Claim 1, wherein the dried thickness of the support is from 10 to 250 micrometers.

20. A recording process as claimed in Claim 1, wherein the transparent protective resin film comprises a polyester resin.

21. A recording process as claimed in Claim 1, wherein the dry thickness of the transparent protective resin film is from 0.01 to 200 micrometers.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/05369

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M7/00 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 780 348 (M.YAMAMOTO ET AL.) 25 October 1988 see column 2, line 65 - column 4, line 55 see figures 1-2; examples 1-4	1-21
X	US,A,4 756 963 (M.YAMAMOTO ET AL.) 12 July 1988 see column 6, line 41 - column 7, line 11 see claim 1; figures 1-3B; examples 1-5	1-21
X	PROCEEDINGS OF THE THIRD INTERNATIONAL CONGRESS ON ADVANCES IN NON-IMPACT PRINTING TECHNOLOGIES, 24 August 1986, SAN FRANCISCO, U.S.A. pages 246 - 251 E.SUZUKI 'A LIGHT-FAST INK-JET FULL COLOUR PRINT WITH FILM LAMINATION.' see page 246, line 22 - page 247, line 13	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 July 1995	28.07.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Bacon, A A.S. Bacon

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

...formation on patent family members

Interr nal Application No
PCT/US 95/05369

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4780348	25-10-88	JP-A- 62130873	13-06-87
US-A-4756963	12-07-88	JP-B- 6053436	20-07-94
		JP-A- 62059076	14-03-87